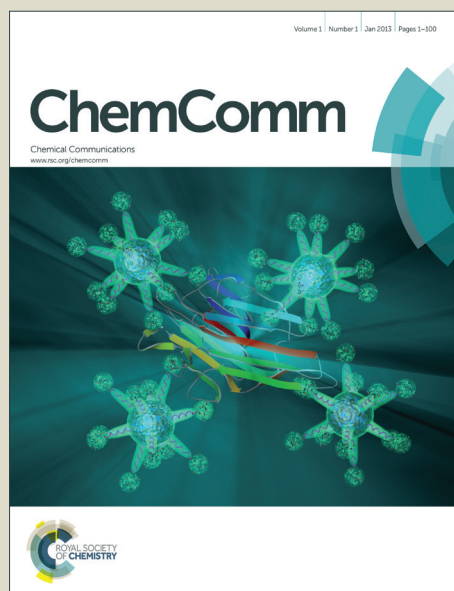


ChemComm

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: X. Ma, Y. Zhang, Y. Zheng, Y. Zhang, X. Tao, Y. Che and J. Zhao, *Chem. Commun.*, 2015, DOI: 10.1039/C5CC00365B.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Highly Fluorescent One-handed Nanotubes from a Chiral Asymmetric Perylene Diimide

Xiaojie Ma^{a,†}, Yibin Zhang^{a,†}, Yingxuan Zheng^a, Yifan Zhang^a, Xia Tao^b, Yanke Che^{a*}, Jincai Zhao^a

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Highly fluorescent bilayer nanotubes with right- or left-handed helical sense were assembled from a chiral asymmetric perylene diimide for the first time, which constitute a new family member of self-assembled organic nanotubes.

Nanotubular assembly of organic molecules has attracted intense interest because of the potential applications in biomimetic systems,¹⁻³ optically active materials,⁴⁻⁶ among others.⁷⁻¹⁰ Although various organic nanotubes have been constructed from synthetic molecular systems including macrocyclic molecules,^{6,11-15} aromatic amphiphiles,¹⁶⁻¹⁹ and oligopeptides,^{1,20,21} perylene diimide (PDI) molecules, a typical and critical class of n-type organic semiconductors,²²⁻²⁸ have not ever been constructed into nanotubes in a controlled approach, despite occasional formation of nanotubes in some kinetic system.²⁹

Recently, we reported that an asymmetric PDI molecule bearing deliberately designed 3,5-dimethoxybenzyl as the polar side chain could be assembled into thermodynamically stable nanocoils.³⁰ On the basis of this finding, we conjecture that the closing-pitch of the helical nanocoils can be achieved for the formation of nanotubular structure through the deliberate control the interplay of the non-covalent interactions of PDI molecules. In this work, we report a new family member of self-assembled organic nanotubes, i.e., the highly fluorescent one-handed nanotubes self-assembled from a chiral asymmetric PDI as shown in Figure 1. We demonstrate that chiral molecule **1** initially forms the nanoribbons that subsequently roll up into racemic nanocoils and nanotubes; a stereochemical bias from the chiral polar side chain slowly gives rise to the transition from the racemic nanotubes, i.e., both right-handed and left-handed nanotubes, to the single-handed form. The single handedness of the resulting nanotube is confirmed by the result that only one-handed nanocoils form during the unwinding of the nanotubes. Furthermore, these one-handed nanotubes are highly emissive, with a fluorescence quantum yield greater than 46%, thereby offering promising applications in optoelectronics, fluorescent sensors, and biological imaging.

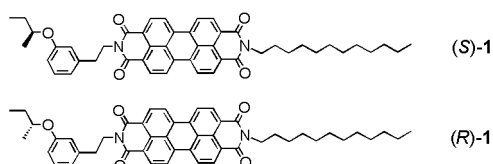


Figure 1 Molecular structures of chiral molecule 1.

The detailed synthesis of chiral molecule **1**, which bears a point chirality in the polar side chain and dodecyl as the other side chain (Figure 1), is described in the Supporting Information (see Scheme S1 in the supporting information). Typically, the self-assembly of (S)-**1** into well-defined nanotubes was achieved through the injection of 0.5 mL of a chloroform solution of (S)-**1** (0.14 mM) into 5 mL of ethanol followed by aging for more than 3 hours. Insight into the nanotubular morphology of (S)-**1** was gained using microscopic techniques. Transmission electron microscopy (TEM) clearly revealed the formation of nanotubes with a uniform diameter from (S)-**1**, as shown in Figure 2a. The formed nanotubes from (S)-**1** are several micrometers long (see Figure S1 in the supporting information) and have a uniform external diameter of 17 nm. A closer examination of the magnified TEM image of a single nanotube shows that the wall thickness of the nanotube is determined to be ca. 4 nm (Figure 2b), indicative of a bilayer structure of the (S)-**1** molecules. Notably, the self-assembly of enantiomer (R)-**1** results in nanotubes with almost the same dimensions (Figure 2c and Figure 2d). Importantly, it is the first time to assemble PDI into the uniform nanotubes in a controlled way, which constitutes a new family member of self-assembled organic nanotubes.^{1-13,16-21}

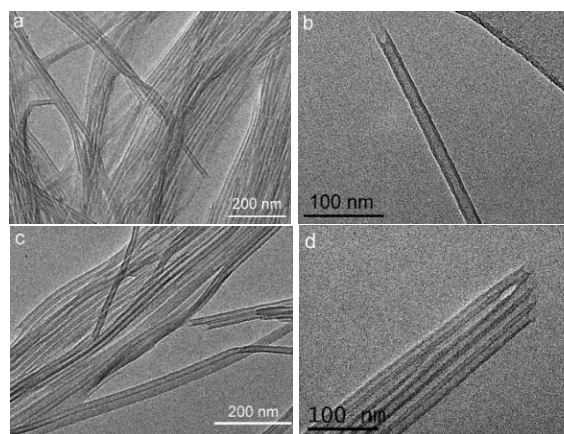


Figure 2 (a) TEM image of the nanotubes assembled from (S)-**1** at 7 days after the initiation of self-assembly. (b) A magnified TEM image of a single nanotube assembled from (S)-**1**. (c) TEM image of the nanotubes assembled from (R)-**1** at 7 days after the initiation of self-assembly. (d) A magnified TEM image of nanotubes assembled from (R)-**1**.

To investigate the mechanism of nanotube formation, we used TEM to monitor the aggregates formed at the early self-assembly process of (S)-**1**. As illustrated in Figure 3a, when a mixture of 0.5 mL of (S)-**1** in chloroform (0.1 mM) and 5 mL of ethanol was
 5 instantaneously measured by TEM, both partially coiled or coiled and tubular aggregates were observed. After 3 h of self-assembly, all of the coils disappeared and only the nanotubes were observed (Figure 3b). The observation of the different intermediates from partially coiled to coiled to tubular aggregates indicates that the
 10 helical coils formed by rolling up an initially formed bilayer nanoribbon are the topological precursors for the nanotubes in the self-assembly process (Figure 3c). Compared to the PDI molecule with 3,5-dimethoxybenzyl as the polar side chain that formed stable nanocoils,³⁰ molecule **1** bearing the ethylene linker and 3-(sec-butoxy) substituent may provide more freedom for the
 15 intermolecular rotation within π -stack and the enhanced interaction for pitch closing, respectively. The helical molecular arrangement of **1** with a larger rotation within the nanotube is supported by absorption and fluorescence spectra (Figure S2), in which an absorption band and a fluorescence maximum are red-shifted by 50 nm and 55 nm compared with those of the individual,
 20 respectively. Compared to the nanocoils previously reported,³⁰ the nanotubes have considerably less red-shifted absorption and fluorescence spectra, suggesting that molecule **1** adopts a helical arrangement with a larger rotation and thus results in weaker electron coupling between neighbour molecules. Such a large
 25 intermolecular rotation is expected to promote a transition from the lowest excited state to the ground state, thereby favoring the luminescence property.^{23,31} Indeed, a fluorescence quantum yield of greater than 46% (as determined from calibrated integrating
 30 sphere measurements) was observed over the nanotubes from **1**, which is much higher than that (ca. 25%) of the nanocoils previously reported.³⁰

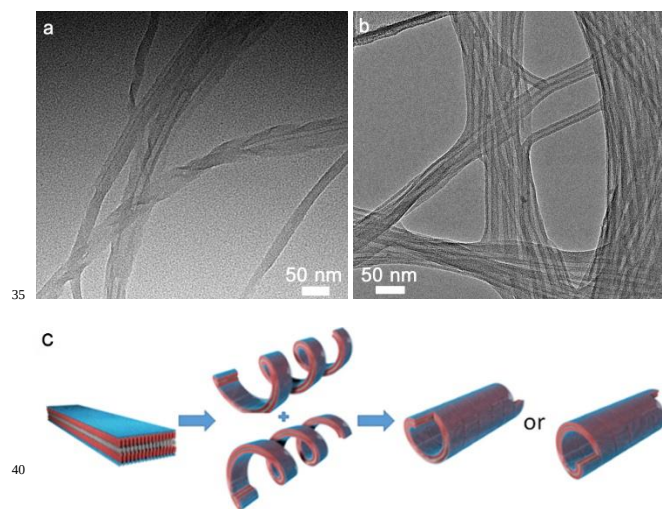


Figure 3 (a) TEM image of the nanotubes assembled from (S)-**1** at 5 min after the initiation of self-assembly. (b) TEM image of the nanotubes assembled from (S)-**1** at 3 h after the initiation of self-assembly. (c) Schematic illustration of the formation of single-handed nanotubes from **1**.

Interestingly, the initially formed nanocoils and nanotubes from (S)-**1** were silent in the circular dichroism (CD) spectra as shown

in Figure 4a. This is consistent with the formation of both right-handed and left-handed helical coils (Figure S3) that racemize their
 50 CD signals. When only nanotubes formed after 3 h of self-assembly, positive CD signals in the range of 460–660 nm began to emerge and gradually increased in intensity with time (Figure 4a), indicative of the transition from racemic nanotubes to the single-handed nanotubes. This CD result also indicates that the molecular
 55 rearrangement by a stereochemical bias for the optically active property mainly occurs in the nanotube, not in the initially formed helical coils. The enantiomer (R)-**1** exhibited a mirror image of the CD spectral profile observed in (S)-**1** during the self-assembly process (Figure 4b). Notably, the final chirality of the nanotube
 60 from either (S)-**1** or (R)-**1** suspending in ethanol remains unaltered over a month, indicating that the optically active nanotubes are thermodynamically stable in solution.

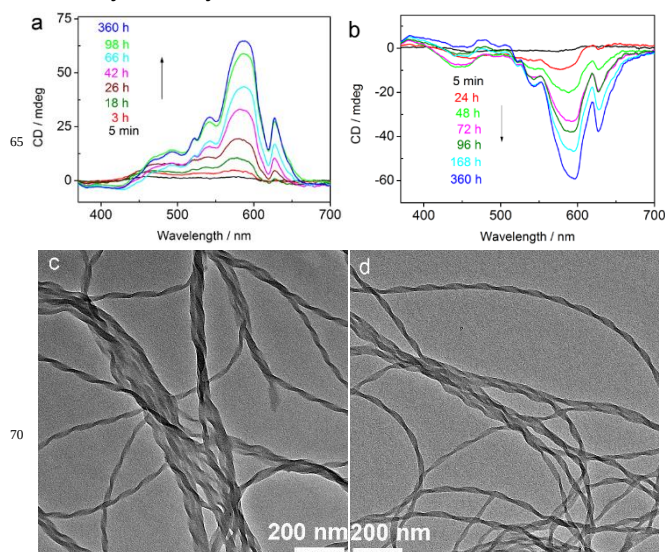


Figure 4 (a), (b) Time-dependent changes in the CD spectra of (S)-**1** and (R)-**1**, respectively, measured in a mixed solvent of 0.5 mL of a chloroform solution of 0.1 mM **1** in 4 mL of ethanol. (c), (d) TEM image of the nanotubes of (S)-**1** and (R)-**1** unwound in acetonitrile for 9 days, respectively.

To confirm whether racemic nanotubes, i.e., coexistence of right-handed and left-handed nanotubes, completely transform into the single-handed nanotubes, we unwound the nanotubes formed after
 80 1 days of self-assembly into the nanocoils whose helical sense can be easily confirmed. Typically, the formed nanotubes were dropped into acetonitrile and aged for 9 days to allow the unwinding of the nanotubes. As shown in Figures 4c and 4d, all the nanotubes assembled from (S)-**1** transformed into left-handed
 85 nanocoils, while those assembled from (R)-**1** transformed into right-handed nanocoils. These results allow us to conclude that the racemic nanotubes initially formed in the self-assembly of (S)-**1** and (R)-**1** completely transformed into left-handed nanotube and right-handed nanotube, respectively, via a stereochemical bias of the chiral PDI molecule. The resulting one-handedness PDI nanotube is also reminiscent of other chiral nanotubular systems,
 90 as elaborately described in the literature.⁷

In conclusion, we, for the first time, reported PDI-based nanotubes with single handedness, i.e., left-handed nanotube assembled from
 95 (S)-**1** or right-handed nanotube assembled from (R)-**1**. We have

confirmed the single handedness of the thermodynamic nanotubes because they were unwound into only one-handed nanocoils. Notably, these one-handed nanotubes are highly emissive, with a fluorescence quantum yield greater than 46%, thereby offering promising applications in optoelectronics, fluorescent sensors, and biological imaging.

This work was supported by NSFC (Nos. 21137004, 21221002, 21322701), the "Youth 1000 Talent Plan" Fund, and the "Strategic Priority Research Program" of the Chinese Academy of Sciences (No. XDA09030200).

Notes and references

^a Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China. E-mail: ykche@iccas.ac.cn

^b State Key Laboratory of Organic-Inorganic Composites, Beijing

University of Chemical Technology, Beijing 100029, China

† Electronic Supplementary Information (ESI) available: Details of the synthesis of molecules **1** and their self-assembly and unwinding. TEM images and optical spectra. See DOI: 10.1039/b000000x/

‡ These authors contributed equally to this work.

- 1 T. Shimizu, M. Masuda and H. Minamikawa, *Chem. Rev.*, 2005, **105**, 1401.
- 2 H. Engelkamp, S. Middelbeek and R. J. M. Nolte, *Science*, 1999, **284**, 785.
- 3 H. Shao, T. Nguyen, N. C. Romano, D. A. Modarelli and J. R. Parquette, *J. Am. Chem. Soc.*, 2009, **131**, 16374.
- 4 W. Jin, T. Fukushima, M. Niki, A. Kosaka, N. Ishii and T. Aida, *Proc. Natl. Acad. Sci.*, 2005, **102**, 10801.
- 5 T. Verbiest, S. Van Elshocht, M. Karuanen, L. Heliemans, J. Snauwaert, C. Nuckolls, T. J. Katz and A. Persoons, *Science*, 1998, **282**, 913.
- 6 Z. Huang, S.-K. Kang, M. Banno, T. Yamaguchi, D. Lee, C. Seok, E. Yashima and M. Lee, *Science* 2012, **337**, 1521.
- 7 T. G. Barclay, K. Constantopoulos and J. Matison, *Chem. Rev.*, 2014, **114**, 10217.
- 8 G. Roelfes and B. L. Feringa, *Angew. Chem., Int. Ed.*, 2005, **44**, 3230.
- 9 T. Yamamoto and M. Sugimoto, *Angew. Chem., Int. Ed.*, 2009, **48**, 539.
- 10 H.-J. Kim, T. Kim and M. Lee, *Acc. Chem. Res.*, 2011, **44**, 72.
- 11 G. D. Pantos, P. Pengo and J. K. M. Sanders, *Angew. Chem., Int. Ed.*, 2007, **46**, 194.
- 12 Y. Yang, W. Feng, J. Hu, S. Zou, R. Gao, K. Yamato, M. Kline, Z. Cai, Y. Gao, Y. Wang, Y. Li, Y. Yang, L. Yuan, X. C. Zeng and B. Gong, *J. Am. Chem. Soc.*, 2011, **133**, 18590.
- 13 H.-J. Kim, S.-K. Kang, Y.-K. Lee, C. Seok, J.-K. Lee, W.-C. Zin and M. Lee, *Angew. Chem., Int. Ed.*, 2010, **49**, 8471.
- 14 D. Pasini and M. Ricci, *Curr. Org. Synth.*, 2007, **4**, 59.
- 15 M. Caricato, A. Delforge, D. Bonifazi, D. Dondi, A. Mazzanti and D. Pasini, *Org. Biomol. Chem.*, 2015, DOI: 10.1039/C4OB02643H.
- 16 Y. Yamamoto, T. Fukushima, Y. Suna, N. Ishii, A. Saeki, S. Seki, S. Tagawa, M. Taniguchi, T. Kawai and T. Aida, *Science*, 2006, **314**, 1761.
- 17 D. M. Eisele, C. W. Cone, E. A. Bloemsmas, S. M. Vlaming, C. G. F. van der Kwaak, R. J. Silbey, M. G. Bawendi, J. Knoester, J. P. Rabe and D. A. Vanden Bout, *Nat. Chem.*, 2012, **4**, 655.
- 18 H. Shao, J. Seifert, N. C. Romano, M. Gao, J. J. Helmus, C. P. Jaronec, D. A. Modarelli and J. R. Parquette, *Angew. Chem., Int. Ed.*, 2010, **49**, 7688.
- 19 A. C. Coleman, J. M. Beierle, M. C. A. Stuart, B. Macia, G. Caroli, J. T. Mika, D. J. van Dijken, J. Chen, W. R. Browne and B. L. Feringa, *Nat. Nanotechnol.*, 2011, **6**, 547.
- 20 I. W. Hamley, *Angew. Chem., Int. Ed.*, 2014, **53**, 6866.
- 21 L. C. Palmer and S. I. Stupp, *Acc. Chem. Res.*, 2008, **41**, 1674.
- 22 F. Würthner, *Chem. Commun.*, 2004, 1564.
- 23 F. Würthner, T. E. Kaiser and C. R. Saha-Moeller, *Angew. Chem., Int. Ed.*, 2011, **50**, 3376.
- 24 C. R. Newman, C. D. Frisbie, D. A. da Silva Filho, J.-L. Bredas, P. C. Ewbank and K. R. Mann, *Chem. Mater.*, 2004, **16**, 4436.

- 25 L. Zang, Y. Che and J. S. Moore, *Acc. Chem. Res.*, 2008, **41**, 1596.
- 26 M. R. Wasielewski, *Acc. Chem. Res.*, 2009, **42**, 1910.
- 27 E. Krieg, H. Weissman, E. Shirman, E. Shimon and B. Rybtchinski, *Nat. Nanotechnol.*, 2011, **6**, 141.
- 28 A. C. Grimsdale and K. Mullen, *Angew. Chem. Int. Ed.*, 2005, **44**, 5592.
- 29 Y. Sun, C. He, K. Sun, Y. Li, H. Dong, Z. Wang and Z. Li, *Langmuir*, 2011, **27**, 11364.
- 30 Y. E, X. Ma, Y. Zhang, Y. Zhang, R. Duan, H. Ji, J. Li, Y. Che and J. Zhao, *Chem. Commun.*, 2014, **50**, 13596.
- 31 J. Cornil, D. Beljonne, J.-P. Calbert and J.-L. Bredas, *Adv. Mater.*, 2001, **13**, 1053.